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ORIGINAL ARTICLE

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Behavior of the cellulose microfibril in shrinking woods

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Abstract We measured the longitudinal and tangential shrinking processes in wood specimens from *Chamaecyparis obtuse* Endl. with different microfibril angles (MFAs). The shape of the shrinking curve was compared with the MFA. Only the longitudinal shrinking process of specimens with a small MFA clearly showed nonlinearity, and the degree of nonlinearity increased as the MFA decreased. In contrast, the tangential shrinking process and the longitudinal shrinking process of compressio n wood with a large MFA were linear. The nonlinearity is probably caused by the longitudinal shrinkage of the noncrystalline region of the cellulose microfibril (CMF) in regions of low moisture content during water desorption. When the moisture content is high, the matrix substance in the cell wall begins to dry; however, the shrinkage in the chain direction is restrained by the rigid CMF. As the wood dries further, the noncrystalline region of the CMF embedded in the matrix substance begins to shrink. Because the longitudinal mechanical behavior of wood with a small MFA is greatly affected by a rigid CMF, longitudinal shrinkage increases suddenly at about 10% moisture content; as a result, the shrinking process shows nonlinearity.

Key words Shrinking process · Nonlinearity · Cellulose microfibril · Noncrystalline region · Wood cell wall

Introduction

Wood cell walls can be approximated by a two-phase structure consisting of an isotropic matrix in which cellulose microfibrils (CMFs) are embedded. The concept of the two-phase structure has played an important role in explaining the mechanisms of various mechanical properties of wood at the level of the fine structure of the cell wall.[1,2] It has been reported that some hemicelluloses, e.g., glucomannan, are arranged close to the CMFs, forming the framework of the cell wall.[3,4] On the other hand, the matrix substance, which consists of lignin and nonoriented polysaccharides, e.g., xylan, is basically amorphous and readily adsorbs water because it contains many free hydroxyl groups. Therefore, the mechanical properties of the matrix substance change with moisture content, leading to changes in the mechanical properties of the wood. However, the CMF has noncrystalline regions to some extent. For example, Nishiyama et al.[5] observed a meridional Bragg reflection corresponding to a longitudinal periodicity of 150 nm in deuterated cellulose fibers from ramie using small-angle neutron scattering, and reported that the CMF could be considered to have four to five disordered residues for every 300 residues. Thereby, it is possible that the noncrystalline regions also adsorb some water molecules. To further our understanding of the mechanical properties of wood, it is very important to obtain information not only on the matrix substance, but also on the noncrystalline cellulose.

Some interesting data have been reported about the anisotropic shrinkage of wood. Sadoh and Christensen[6] reported that a longitudinal shrinking process of normal wood of *Araucaria cunninghamii* Ait. shows nonlinearity. Similar phenomena have been observed in other species, e.g., *Pinus radiata*.[7] Because the microfibril angle (MFA) of the S_2 layer, which occupies a large part of the cell wall in normal coniferous wood, is generally small, it seems reasonable to assume that the mechanical property changes in CMFs, as a result of water desorption, would greatly influence the longitudinal shrinking process. Several explanations have been put forward as to the causes of nonlinearity in the longitudinal shrinking process.[7–10] For example, Sadoh and Kingston[10] concluded that nonlinearity is due to decreased slipping of the chain molecules against one another, and that this decrease is caused, in turn, by increasing interchain molecular bonding with reduced moisture content. On the other hand, according to Meylan,[7] it was assumed that the only cause of nonlinearity is a change in the elastic constants as the moisture content changes. In either case, it has

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been hypothesized that the CMF itself is not affected by moisture content. However, as mentioned above, the CMF contains some noncrystalline regions. Therefore, it is important to clarify the cause of nonlinearity, taking into consideration the behavior of the noncrystalline regions in the CMF.

We measured the longitudinal and tangential shrinking processes of specimens with various MFAs (normal, compression, and opposite woods), and examined the relationship between the degree of nonlinearity in the shrinking process and the MFA. The mechanical properties peculiar to the CMF and the matrix substance were examined in specimens with various MFAs. Based on our results, we discuss the structural changes in the CMF during water desorption and propose a cause for nonlinearity in the longitudinal shrinking of wood.

Materials and methods

Samples

All measurements in this study were made on a 25-year-old hinoki (*Chamaecyparis obtuse* Endl.), the trunk of which was crooked near the base. Blocks of compression and opposite wood from the crooked region, and normal wood from the straight region, were sampled. Specimens for the measurement of longitudinal shrinkage [50 (L) × 10 (T) × 5 (R) mm] and tangential shrinkage [10 (L) × 20 (T) × 5 (R) mm] were prepared from each block without drying. All specimens were boiled for 10min to ensure water saturation. For longitudinal shrinkage, we used 20, 7, and 7 specimens of compression, opposite, and normal wood, respectively; for tangential shrinkage, we prepared 18, 10, and 8 specimens, respectively.

Measurement of the shrinking process

All specimens were dried incrementally inside an air-conditioned desiccator with various relative humidities at a room temperature of 20°C. The weight (w) and length (l) of each specimen were measured at each relative humidity (RH). The reading accuracies of an electric balance and a dial gauge comparator (Fig. 1) were 0.1mg and 0.001mm, respectively. The moisture content of the specimen was controlled at 98%, 94%, 76%, 50%, 10%, and 2% RH, using H_2O, KNO_3, NaCl, $Ca(NO_3)_2$, silica gel, and P_2O_5 powder, respectively, as the salts or drying agents. The moisture content of the specimen equilibrated with H_2O was set to the fiber saturation point (FSP). The weight and length under air-dried conditions (25% RH) were also measured inside the desiccator, without the salts or drying agents, before drying with silica gel. After being dried with P_2O_5, each specimen was oven-dried for 24h at 105°C; thereafter, the oven-dry weight (w_0) was measured. The shrinkage of a specimen at each relative humidity was calculated on the basis of the length at FSP (l_0). The moisture content of each specimen was determined from its oven-dry weight and the weight at each relative humidity. Thus, shrinkage (α) and moisture content (M) at each relative humidity were calculated as

$$\alpha = \frac{l_0 - l}{l_0} \times 100(\%), \quad M = \frac{w - w_0}{w_0} \times 100(\%) \qquad (1)$$

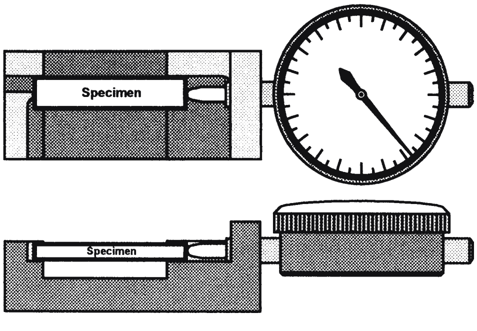

Fig. 1. Schematic illustration of a dial gauge comparator

Measurement of microfibril angle

A flat-sawn section, 0.2mm thick, was prepared with a sliding microtome from earlywood and latewood of each specimen after measuring shrinkage. The microfibril angle of the S_2 layer (MFA) in a section was measured using X-ray diffraction according to the improved Cave's method.[11–13] The average value between the earlywood and latewood sections was used as the MFA for each shrinkage specimen.

Results

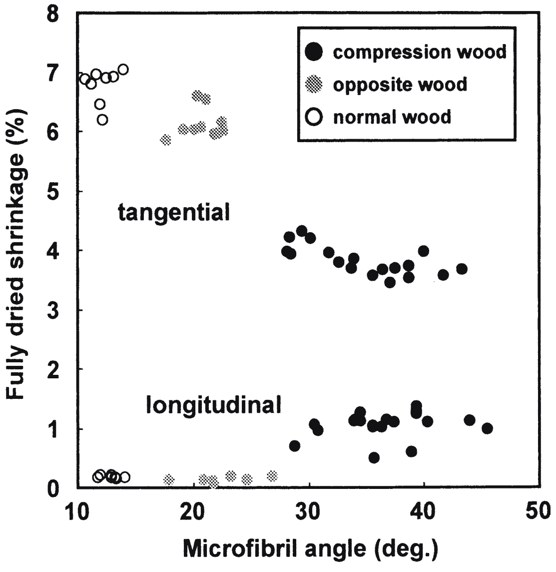

Fig. 2. Relationship between fully dried shrinkage and microfibril angle

Figure 2 shows the relationships between longitudinal and tangential fully dried shrinkages and MFAs, where the fully

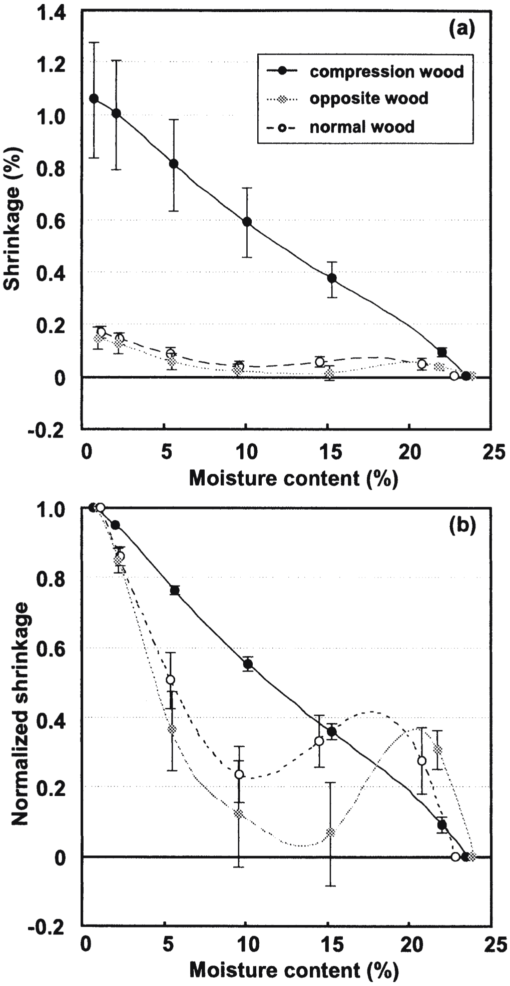

Fig. 3a,b. Longitudinal shrinking processes for compression, opposite, and normal wood. **a** Average; **b** normalized

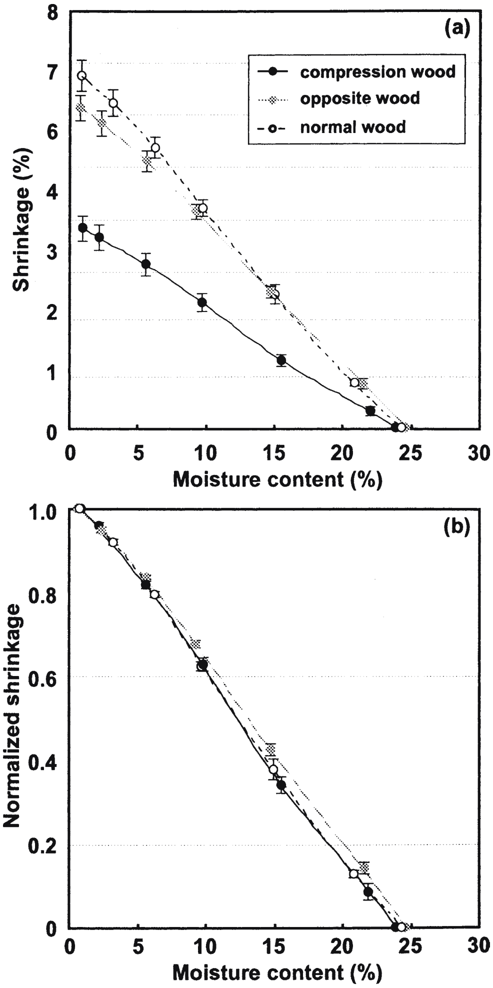

Fig. 4a,b. Tangential shrinking processes for compression, opposite, and normal wood. **a** Average; **b** normalized

dried shrinkage is defined as the shrinkage equilibrated by P_2O_5. In both the longitudinal and tangential shrinkage specimens, the MFA was highest in the compression wood, followed by opposite and normal wood. The longitudinal shrinkages were 0% to 0.2%, regardless of the MFA, when the MFA was below 27°. However, the longitudinal shrinkage showed a remarkable increase when the MFA increased above 27°, and was constant when the MFA was above 35°. This trend is almost in agreement with Yamamoto et al.,[14] while, in contrast, the longitudinal shrinkage reported by Meylan[15] showed a steep increase with MFA, even in the large-MFA region. On the other hand, the tangential shrinkage decreased linearly when the MFA was below 35°, although it remained nearly constant above 35°.

Figure 3a shows the average longitudinal shrinking processes for compression, opposite, and normal wood. As shown in this figure, the normal and opposite wood seldom shrank longitudinally until a moisture content of 10% was reached, although slight shrinkages were observed at about 22%. Both types of wood shrank suddenly below 10% moisture content. However, the shrinking curve of compression wood with a large MFA became nearly linear over the entire range of moisture contents. Figure 3b illustrates the normalized shrinking processes by fully dried shrinkage. This figure clarifies the rapid increase in longitudinal shrinkage observed in normal and opposite wood when the moisture content was below 10%. Strictly speaking, the longitudinal shrinkages of normal and opposite woods were not constant above 10%, i.e., they tended to increase when the moisture content decreased from the FSP to 22%, and then decreased until 10% was reached.

Figure 4a shows the average tangential shrinking processes for compression, opposite, and normal wood. Figure 4b shows the normalized tangential shrinking processes. As shown in these figures, all tangential shrinking processes were approximately linear, regardless of MFA.

Discussion

The above results indicate that only the longitudinal shrinking processes of normal and opposite wood show nonlinearity, i.e., a remarkable increase in shrinkage occurs below 10% moisture content. For specimens with small MFAs, the CMF with high rigidity probably affects the longitudinal mechanical properties of the wood. Thus, we expected that the observed nonlinearity is caused by an abrupt change in the qualitative properties of the CMF itself during water desorption, especially at low moisture content, and then such an abrupt change becomes actualized in specimens with a small MFA. To verify this expectation, we defined the degree of nonlinearity of the shrinking process and compared it with the MFA.

The degree of nonlinearity of a shrinking process (N) is defined as

$$N = \frac{\int_{\mathrm{FDP}}^{\mathrm{FSP}} \left| g(x) - f(x) \right| dx}{\int_{\mathrm{FDP}}^{\mathrm{FSP}} \left| g(x) \right| dx}, \qquad (2)$$

where x is moisture content, $f(x)$ is the cubic spline interpolation of the shrinking process data, and $g(x)$ is the straight line that connects the FSP to the fully dried point (FDP) in the shrinking process. A larger value of N means that the shrinking process is becoming increasingly nonlinear, whereas it becomes more linear as N approaches zero.

Figure 5 shows the relationships between the degree of nonlinearity (N) and MFA. As shown in Fig. 5a, the value of N approaches zero when the MFA is above 30°. This means the longitudinal shrinking process is almost linear in specimens with a MFA larger than 30°; on the other hand, N increases as the MFA decreases below 30°. The value of N in the longitudinal shrinkage of opposite wood is greater than that of normal wood, and the dispersion is also larger. The reason for this large dispersion is probably that the longitudinal dimension of opposite wood varies considerably more than that of normal wood at high moisture content. On the other hand, N in tangential shrinkage becomes almost zero, regardless of the MFA (Fig. 5b). The high degree of non-linearity observed in the longitudinal shrinking process of specimens with a small MFA supports the hypothesis that an abrupt change occurs in the CMF in regions of low moisture content.

We considered the following mechanism on the behavior of the CMF and the matrix substance during water desorption. In regions of high moisture content, water desorption probably occurs mainly in the matrix substance; therefore, because the CMF is embedded in the matrix substance, only the matrix substance tends to shrink. However, in wood specimens with a small MFA, the adjacent microfibrils restrain the free shrinkage of the matrix substance to some extent, especially in the chain direction of the CMF. As shown in Figs. 3–5, the longitudinal shrinkage of normal or opposite wood is almost zero when the moisture content exceeds 10%. As the wood dries further, water molecules in the matrix substance are lost. The noncrystalline region of the CMF embedded in the matrix substance then desorbs water molecules and begins to shrink, causing the specimen to rapidly shrink longitudinally when the moisture content is below 10%. Clair and Thibaut[16] observed the longitudinal shrinkage of the gelatinous layer in poplar and beech tension wood, and pointed out that "hygrosensible zones" in the CMF seem to cause the longitudinal shrinkage of the CMF. Their report supports the longitudinal shrinkage of the noncrystalline region in the CMF. Moreover, the longitudinal shrinkage of normal wood, which contains more cellulose and a smaller MFA than compression wood, is greatly influenced by the longitudinal shrinkage of the CMF. On the other hand, it is probable that tangential shrinkage and longitudinal shrinkage of specimens with a large MFA show linearity because of the dominant contribution of the matrix substance to shrinkage.

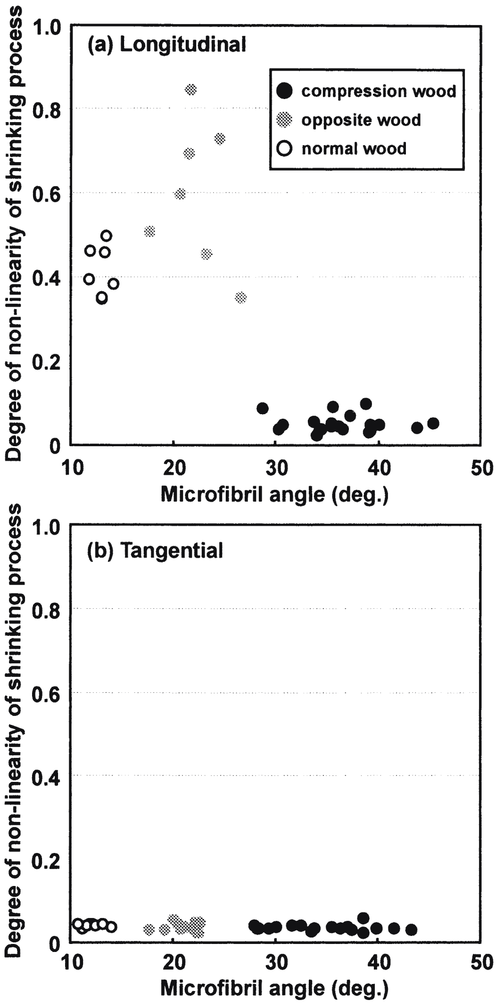

Fig. 5a,b. Relationship between the degree of nonlinearity of the shrinking process and microfibril angle. **a** Longitudinal; **b** tangential

Conclusions

Some researchers have discussed nonlinearity in the longitudinal shrinking process theoretically, and assumed in their theories that CMF is not influenced by moisture adsorption. However, the fact that nonlinearity in the longitudinal shrinking process is prominent in normal and opposite wood with small MFAs (Fig. 5a) suggests that the CMF begins to shrink in its axial direction when the moisture content is low. Consequently, the longitudinal shrinkage of wood specimens with a small MFA rapidly increases when the moisture content is below 10%, and the process shows nonlinearity.

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